REACTIVE INTERMEDIATES IN CATALYTIC COPROCESSING

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INTRODUCTION

Fundamental studies of the mechanism of catalytic coal con-
version not only provide an understanding of how current cata-
lysts work but also offer the prospect of designing better cata-
lysts in the future. One approach to the study of catalysis is to
observe the production of products from single, known probe com-
pounds. This approach is especially useful when the products can
be shown to arise only from particular reactive intermediates,
such as cations or radicals.

Three probes were used to investigate the mechanism of
catalysis of a dispersed molybdenum sulfide catalyst. The 1,5-
dimethylnaphthalene (1,5-DMN) was selected because of its ability
to distinguish three important types of reactions (Figure 1).
Under cationic conditions, the methyl groups of 1,5-DMN migrate
to form 1,6-DMN and subsequently 2,6-DMN.[1] Each isomer will react
to give an equilibrium mixture of all three isomers, but the 1,5-
DMN is the least stable and thus is the most sensitive probe for
a cationic environment. The 1,5-DMN can also undergo demethyla-
tion to form 1-methylnaphthalene (1-MN). This reaction can be
envisioned as occurring either via a cationic cracking mechanism
or via an ipso substitution by a hydrogen atom; however, the evi-
dence given below supports a radical ipso substitution under our
conditions. The third reaction of 1,5-DMN is hydrogenation. This
leads to the formation of 1,5-dimethyltetralin (1,5-DMT). Thus,
three reaction types of interest in catalytic coal conversion are
distinguished by this probe. In addition, decalin and tricyclo-
decane (Figure 2) were used to distinguish hydrogen abstraction
reactions. The results obtained from these three probes provide a
description of the reaction environment present during catalytic
coprocessing.

Other workers at the PETC[2] have shown molybdenum trisulfide
prepared by the method of Eggertsen and Roberts[3] to be an effec-
tive coprocessing catalyst. Reactions of the probe compounds in
the presence of this catalyst were compared to the reactions
observed in the presence of a known cationic catalyst and a known
radical initiator. These reference additives were selected to
ensure that the probes would indeed distinguish the different
reaction environments. Bibenzyl generates free radicals by a
thermolytic dissociation to form stoichiometric amounts of benzyl

radicals.[4] These radicals abstract hydrogen from solvent and solute, and thus provide a pool of radicals of varying activity. Benzyl radicals also abstract hydrogen atoms from gas phase hydrogen, producing hydrogen-atom-mediated hydrocracking.[4] A commercial cracking catalyst (D980-13) was selected because of the known acidic character of silica-alumina catalysts.[5] Thus, a comparison of the reactions of the probes in the presence of the molybdenum sulfide with the reactions in the presence of the reference additives provides information about the reaction environment generated by the coprocessing catalyst.

EXPERIMENTAL

The commercial silica alumina (D980-13) was obtained from W.R. Grace (grade 980-13, 13% alumina) as an extrudate. The friable solid was ground with a mortar and pestle, and oven-dried at 150°C overnight. The molybdenum trisulfide was prepared from ammonium tetrathiomolybdate by precipitation from an aqueous solution using formic acid.[3] This procedure is best carried out in a hood because of the hydrogen sulfide formed.

All reactions were performed using 40-mL 316-stainless steel reactors. The 8-gram reaction mixtures contained the probe (200 mg); a silica-alumina (10 mg), molybdenum trisulfide (10 mg), or bibenzyl (2.0 g) additive; and n-octacosane solvent. The reactors were pressurized to 1200 psig with hydrogen, heated to 425°C within 5-6 minutes by plunging them into a preheated fluidized sand bath, and shaken at temperature for 60 minutes. The products were washed from the cooled reactor using inhibitor-free tetrahydrofuran (Aldrich 27,038-5) and were analyzed by GC-MS.

RESULTS

The reactions of 1,5-DMN are shown in Figure 1. The amounts of the products obtained in the presence and absence of the three additives are given in Table I. The effect of the added bibenzyl is to increase the yield of 1-MN because of the increased production of hydrogen atoms.[4] Significantly, no isomerization of the methyl groups is seen in the blank or in the presence of the free radical initiator, nor is the hydrogenation to 1,5-DMT an important reaction under these conditions. In the presence of the acidic catalyst, D980-13, the isomerization of the methyl groups becomes the predominate reaction. Of the recovered dimethylnaphthalenes, 83% have at least one methyl group in a beta position. The 1,5-DMN is indeed sensitive to the presence of the acidic sites of this catalyst. Both 1-MN and 2-MN are obtained as the demethylated products. The total amount of demethylation is the same as was seen in the absence of catalyst, about 10%. In this case, it is reasonable to assume that the cationic mechanism is superimposed on the background radical reaction. The

1,5-DMN can rearrange via a cationic mechanism, and the isomers thus produced can subsequently crack by a hydrogen atom mechanism. In addition, the 1-MN and 2-MN formed from the cracking can be interconverted by the acid catalyst. Again, no effect is seen on the amount of hydrogenation, which remains low. The results obtained in the presence of the molybdenum trisulfide catalyst are shown in the last column of Table I. Molybdenum disulfide is assumed to be the actual form of the catalyst under liquefaction-like conditions.[3] The effect of adding this catalyst is to increase the extent of hydrogenation to form the dimethyltetralin. The molybdenum catalyst does not exhibit cationic behavior, as evidenced by the lack of isomerization of the methyl groups, nor does it increase the extent of hydrocracking to form methylnaphthalene. The lack of cationic activity was initially surprising because single crystal experiments at lower temperatures have associated carbonium ion intermediates with the basal plane of molybdenum disulfide.[6] However, a similar lack of isomerization has been noted during the cracking of 1-methylnaphthalene in the presence of a supported CoMo catalyst at slightly higher temperatures.[7]

In addition to the aromatic hydrocarbon probe, two alicyclic hydrocarbons, decalin and tricyclo[5.2.1.0^{2,6}]decane (TCD), were used as probes (Figure 2). The isomerization of cis- to trans-decalin requires the removal of a tertiary hydrogen, whereas the isomerization of endo- to exo-TCD requires the removal of a secondary hydrogen.[8] The ratios of the isomers (more stable / less stable) after reaction in the presence and absence of the three additives are given in Table II. The effect of added bibenzyl is to increase the extent of isomerization of both probes. The radical isomerization of the decalin is known to occur under these conditions,[9] but the radical isomerization of the TCD was surprising. In general, Wagner-Meerwein rearrangements are not observed for radicals. One exception is the recently reported radical isomerization of homoadamantane to methyladamantane.[10] The addition of the D980-13 acidic catalyst had no effect on the isomerization of the TCD, but it did cause an increase in the extent of the isomerization of the decalin. Apparently the decalin can isomerize by either hydrogen atom or hydride abstraction. The results obtained from the molybdenum sulfide are very similar to the results from the D980-13 catalyst for this set of probes. The isomerization of the TCD is unaffected, but the isomerization of the decalin is accelerated.

DISCUSSION

The results obtained from the three probes are summarized in Table III. The catalysts are considered to either promote (+) or not promote (-) the reactions listed. Aromatic methyl group hydrocracking is promoted only by bibenzyl and is thus proceeding via an ipso substitution by a hydrogen atom.[4] The lack of crack-

ing in the presence of the D980-13 catalyst is likely due to the difficult formation of methyl cations. The isomerization of endo-TCD is also catalyzed only by the bibenzyl and is therefore proceeding via a radical hydrogen abstraction from a secondary carbon. If free radicals are formed in the presence of the molybdenum sulfide, they are not energetic enough to react with gas phase hydrogen to form the hydrogen atoms, nor are they energetic enough to abstract the secondary hydrogen from the TCD. This means they have to be considerably less reactive than the benzyl radicals formed from the bibenzyl.

Since the isomerization of the 1,5-DMN is catalyzed only by the D980-13 acidic catalyst, it is probably proceeding via a cationic mechanism, similar to that found in the presence of solution phase acids.[1] The absence of this isomerization for the molybdenum sulfide indicates either that there are few acid sites of sufficient strength to catalyze the isomerization, or that the active sites are not accessible to the 1,5-DMN. Other sites of lower acidity may be present.

All three additives are capable of increasing the amount of isomerization of decalin. At least two mechanisms are operative. In the presence of a radical initiator, the isomerization is driven by the abstraction of a hydrogen atom from the tertiary carbon.[9] In the presence of the acid catalyst, a similar mechanism involving hydride abstraction would account for the increased isomerization. Isomerization occurs also in the presence of the molybdenum sulfide. Since the molybdenum catalyst shows no activity in the other radical and cationic reactions above, it may be catalyzing the isomerization by yet a third mechanism. Dehydrogenation of the cis-decalin by loss of one tertiary hydrogen and an adjacent secondary hydrogen leads to an octalin with the double bond to the bridgehead carbon. Subsequent hydrogenation from the opposite side leads to the trans-decalin. The feasibility of a dehydrogenation – hydrogenation mechanism is strengthened by the observed hydrogenation activity described next.

Only the molybdenum sulfide was effective in hydrogenating the naphthalene ring to form tetralin. The absence of concomitant radical or cationic reactions indicates that the hydrogenation is probably proceeding via a surface-bound intermediate or a concerted addition of hydrogen. Based on the information provided by these probes, the effectiveness of the molybdenum sulfide catalyst in coprocessing may lie in the fact that it provides hydrogenation activity but does not introduce strong acid sites associated with coke formation nor does it promote radical formation, which has been associated with retrogressive reactions. The possible presence of weaker acid sites, capable of cracking other alkyl chains, is being investigated.

CONCLUSIONS

Probe compounds have been used to explore the mechanism of catalysis of a molybdenum sulfide known to be active for the co-processing of coal and oil residua. Under typical coprocessing conditions, the sulfide displayed predominately hydrogenation activity. Comparison with additives known to be sources of radical and cationic activity provided no evidence that the molybdenum catalyst has either of these properties.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the U.S. Department of Energy.

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TABLE I. Normalized Distribution of Products from 1,5-Dimethyl-naphthalene.

		ADDITIVE		
	None	Bibenzyl	D980-13	MoS_3
1,5-DMN	83%	48%	15%	66%
1,6-DMN	1%	1%	38%	3%
2,6-DMN	0	1%	33%	0
1-MN	13%	38%	6%	14%
2-MN	0	1%	8%	0
NAP	0	8%	0	1
DMT	4%	2%	0	17%

Note: DMN = Dimethylnaphthalene
      MN = Methylnaphthalene
      NAP = Naphthalene
      DMT = Dimethyltetralin

TABLE II. Comparison of the Extent of Isomerization of cis-Decalin and endo-Tricyclo[5.2.1.0^{2,6}]decane.

	TCD	DECALIN
CATALYST	EXO / ENDO	TRANS / CIS
None	0.31	0.29
Bibenzyl	1.38	2.33
D980-13	0.33	0.91
MoS_3	0.28	1.13

TABLE III. Summary of Probe Reactions.

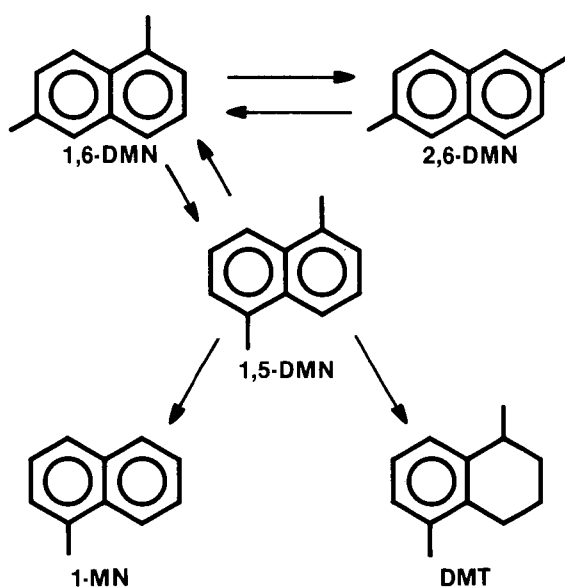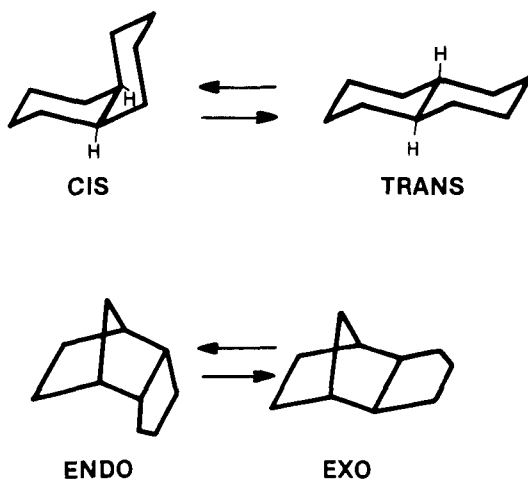|	Bibenzyl	D980-13	MoS_3
Methyl-Group Hydrocracking	+	-	-
Isomerization at 2° Carbon	+	-	-
Isomerization of Aromatic Alkyl-Group	-	+	-
Isomerization at 3° Carbon	+	+	+
Hydrogenation	-	-	+

FIGURE 1. REACTIONS OF 1,5-DIMETHYLNAPHTHALENE.

FIGURE 2. THE ISOMERIZATION OF DECALIN AND TRICYCLO[5.2.1.0^{2,6}]DECANE.